

Higher order and infinite Trotter–number extrapolations in path integral Monte Carlo

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(Dated: February 2, 2008)

Abstract

Improvements beyond the primitive approximation in the path integral Monte Carlo method are explored both in a model problem and in real systems. Two different strategies are studied: the Richardson extrapolation on top of the path integral Monte Carlo data and the Takahashi-Imada action. The Richardson extrapolation, mainly combined with the primitive action, always reduces the number-of-beads dependence, helps in determining the approach to the dominant power law behavior, and all without additional computational cost. The Takahashi-Imada action has been tested in two hard-core interacting quantum liquids at low temperature. The results obtained show that the fourth-order behavior near the asymptote is conserved, and that the use of this improved action reduces the computing time with respect to the primitive approximation.

PACS numbers: 31.15.Kb, 02.70.Ss

I. INTRODUCTION

Path integral Monte Carlo (PIMC) has become in the last decade a standard tool for studying quantum liquids and solids at finite temperature.^{1–3} The PIMC method allows for the calculation of the quantum-statistical partition function, and from it, thermodynamic functions like the internal energy or the specific heat. The basis on which PIMC rests is the analytical continuation to imaginary time of Feynman’s path-integral formalism of Quantum Mechanics.^{4–6} The resulting convolutive property for the thermal density matrix makes accessible the quantum physics of low temperatures starting from density matrices at higher temperatures. At sufficiently high temperature, commutator terms between the kinetic and potential operators defining the Hamiltonian of the system can be disregarded, and then, the density matrix factorizes as a product of the kinetic and potential parts. This is known as the primitive approximation (PA) and the unbiased convergence to a desired lower temperature by increasing the number M of convolutive terms is guaranteed by the Trotter formula.⁷

The expectation value of an operator through the thermal density matrix is written in this language as a multidimensional integral appropriate for a Monte Carlo interpretation. The quantum problem can be mapped to a classical one of interacting polymers, each one representing an atom.^{8,9} In the action, beads of different atoms but with the same index interact through the potential, and all the beads of the same atom form a closed chain of springs. At the level of the PA and avoiding the specific quantum statistics of the atoms or molecules, relevant at temperatures near the absolute zero, the PIMC method looks rather simple. However, in the implementation of the algorithm there are technical aspects which require of some additional effort. The main point is that, as the number of beads of the polymeric chains increases rapidly with decreasing temperature, the sampling of the probability distribution function becomes almost impossible by means of individual movements. Several mechanisms for performing smart collective movements of the beads have been proposed and proved to be able of eliminating the slowing down present in the single-bead schemes. Worth mentioning are the staging^{10–12} and bisection^{2,13} which exploit the fact that the free action (kinetic part in an interacting system) can be sampled by non-rejection methods, and therefore, only the potential part requires a Metropolis step. In a large number of PIMC simulations, these collective sampling schemes are enough to reach a reasonable de-

gree of efficiency. Nevertheless, calculations of quantum fluids at extremely low temperature require chains composed by several thousands of beads, feature which makes the problem more involved.

The number of beads required to achieve the asymptotic regime, at a given temperature, depends on the approximation taken for the action. It has been proved that PA is accurate to order $(\beta/M)^2$, with β the inverse temperature and M the number of beads.^{14,15} Focusing the analysis on PIMC, and thus not considering the specific developments for the Fourier PIMC method,¹⁶ the improvement of the action can be pursued following at least two different alternatives. In the first one, the PA is substituted by the pair-product action in which the basic step on the chain is constructed as the exact action for two isolated atoms.¹⁰ This method is more efficient than the PA, mainly when dealing with hard-sphere-like systems, and it is the only method up to date which has proved to be accurate enough to reach the superfluid regime of liquid ^4He .² The second possibility relies on the inclusion in the action of the lowest-order corrections to the primitive approximation for the exponential of the Hamiltonian $e^{-\beta\hat{H}}$. To this end, Takahashi and Imada¹⁷ and later on, and independently, Li and Broughton¹⁸ found a manageable expression for the trace accurate to order $(\beta/M)^4$. In this approximation, hereafter referred as TIA, the beads of different atoms interact through an effective potential which is the sum of the interatomic potential and a β -dependent term containing the double commutator $[[V, K], V]$, with V and K the potential and kinetic operators, respectively. Recently, Jang *et al.*¹⁹ have used in PIMC a genuine fourth-order factorization according to the proposal of Suzuki²⁰ and the posterior developments of Chin.^{21,22} However, the accuracy achieved in several test problems by Jang *et al.*¹⁹ is comparable to the one reached using the simpler TIA.

In the present paper we analyze the β/M dependence of the energy using both PA and TIA for a test model and for two strongly interacting fluids at low temperature, i.e., Ne and ^4He . In the analysis of the PA results, we introduce the Richardson extrapolation.²³ The efficiency of this numerical scheme for extrapolation is well known in fields like integration or solution of differential equations. We show that its use in PIMC can also be useful in two directions. First, its simple use helps in determining when the expected law $(\beta/M)^2$ is reached; second, the successive extrapolations to $M \rightarrow \infty$ follow a nearly fourth-order dependence and then they always approach faster to the asymptote than the PA. The second main objective of the work is the study of the TIA when applied to hard-core interacting

systems in the regime of low temperatures since the applications of TIA to these situations is rather scarce.^{24–27} Previous tests of the TIA to systems not so dense and not so cold have shown the expected fourth-order accuracy.²⁴ In fact, the achievement of a fourth-order law for hard-core potentials using TIA has been some times questioned² but never thoroughly analyzed. Our present results show that in the regime studied the accuracy obtained is the expected one and the global efficiency of TIA is larger than the one of the standard PA. On the other hand, the use of the Richardson extrapolation on top of the TIA results has proved not to be so helpful, at least in the temperatures where the two real systems have been studied.

The rest of the paper is organized as follows: Section II contains the formalism of the PA and the TIA, including the expressions for the thermodynamic and centroid-virial estimators for the energy. The application of the Richardson extrapolation to the PIMC calculations is also discussed. In Sec. III, results for the three systems under study are presented with special emphasis to the (β/M) dependence of the energy obtained using the two models for the action. Finally, Sec. IV comprises a brief summary and the main conclusions of the work.

II. FORMALISM

The partition function of a system described by a Hamiltonian \hat{H} at a temperature $T = 1/\beta$ is

$$Z = \text{Tr } e^{-\beta \hat{H}}. \quad (1)$$

We consider a system composed by N particles with $\hat{H} = \hat{K} + \hat{V}$, the kinetic operator being

$$\hat{K} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2, \quad (2)$$

and the potential one

$$\hat{V} = \sum_{i < j}^N V(r_{ij}), \quad (3)$$

where pairwise interactions are assumed. The PA is the lowest order term in powers of (β/M) of the exponential of the sum of the two operators \hat{K} and \hat{V} ,

$$\text{Tr } e^{-\beta(\hat{K}+\hat{V})} \simeq \text{Tr } \left(e^{-(\beta\hat{K}/M)} e^{-(\beta\hat{V}/M)} \right)^M. \quad (4)$$

In fact, in the limit where $M \rightarrow \infty$ the previous expression becomes exact, yielding the Trotter formula. With the decomposition (4), and restricting the analysis to distinguishable particles, the partition function becomes

$$Z = \int d\mathbf{R}_1 \dots d\mathbf{R}_M \prod_{\alpha=1}^M \rho_{\text{PA}}(\mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}) , \quad (5)$$

with $\mathbf{R} \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and $\mathbf{R}_{M+1} = \mathbf{R}_1$. Greek and Latin indexes are used throughout the paper to denote beads and particles, respectively. The primitive factorization (4), which decouples the kinetic and potential operators, leads to the well-known PA,

$$\rho_{\text{PA}}(\mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}) = \left(\frac{Mm}{2\pi\beta\hbar^2} \right)^{3N/2} \exp \left\{ - \sum_{i=1}^N \frac{Mm}{2\beta\hbar^2} (\mathbf{r}_{\alpha,i} - \mathbf{r}_{\alpha+1,i})^2 - \frac{\beta}{M} \sum_{i < j}^N V(r_{\alpha,ij}) \right\} . \quad (6)$$

Takahashi and Imada¹⁷ proved that it is possible to extend the accuracy of the action up to fourth order for the trace by substituting in Eq. (4) the operator \widehat{V} by another one \widehat{W} given by

$$\widehat{W} = \sum_{i < j}^N V(r_{ij}) + \frac{1}{24} \frac{\hbar^2}{m} \left(\frac{\beta}{M} \right)^2 \sum_{i=1}^N |\mathbf{F}_i|^2 . \quad (7)$$

The second term on the r.h.s of Eq. (7) corresponds to the double commutator $[[V, K], V]$ appearing in the development of the exponential $e^{-\beta\widehat{H}}$. The classical-like force \mathbf{F}_i is defined as

$$\mathbf{F}_i = \sum_{j \neq i}^N \nabla_j V(r_{ij}) . \quad (8)$$

Therefore, the partition function using the TIA is written like the PA one (5) just substituting the interatomic potential $V(r_{\alpha,ij})$ in Eq. (6) by $W(r_{\alpha,ij})$,

$$\begin{aligned} \rho_{\text{TIA}}(\mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}) &= \left(\frac{Mm}{2\pi\beta\hbar^2} \right)^{3N/2} \exp \left\{ - \sum_{i=1}^N \frac{Mm}{2\beta\hbar^2} (\mathbf{r}_{\alpha,i} - \mathbf{r}_{\alpha+1,i})^2 \right. \\ &\quad \left. - \frac{\beta}{M} \left(\sum_{i < j}^N V(r_{\alpha,ij}) + \frac{1}{24} \frac{\hbar^2}{m} \left(\frac{\beta}{M} \right)^2 \sum_{i=1}^N |\mathbf{F}_{\alpha,i}|^2 \right) \right\} . \end{aligned} \quad (9)$$

First derivatives of the partition function allow for the estimation of the total and partial energies of the N -body system,⁵

$$\frac{E}{N} = -\frac{1}{NZ} \frac{\partial Z}{\partial \beta} \quad (10)$$

$$\frac{K}{N} = \frac{m}{N\beta Z} \frac{\partial Z}{\partial m} \quad (11)$$

and $V/N = E/N - K/N$. The potential energy, and any other coordinate operators, can also be obtained through the general relation¹⁷

$$O(\mathbf{R}) = -\frac{1}{\beta} \frac{1}{Z(V)} \left. \frac{dZ(V + \lambda O)}{d\lambda} \right|_{\lambda=0}. \quad (12)$$

Equation (11) leads to the thermodynamic estimators for the kinetic energy. At the level of PA,

$$\frac{K_{\text{PA}}^{\text{th}}}{N} = \frac{3M}{2\beta} - \sum_{\alpha=1}^M \sum_{i=1}^N \frac{Mm}{2N\beta^2\hbar^2} (\mathbf{r}_{\alpha,i} - \mathbf{r}_{\alpha+1,i})^2. \quad (13)$$

In the case of the TIA the effective potential W depends on the mass of the particles and the temperature. Therefore, explicit terms depending on the interatomic potential appear in the estimation of the kinetic energy. Explicitly,

$$\frac{K_{\text{TIA}}^{\text{th}}}{N} = \frac{K_{\text{PA}}^{\text{th}}}{N} + \frac{1}{24} \frac{\hbar^2}{m} \frac{\beta^2}{NM^3} \sum_{\alpha=1}^M \sum_{i=1}^N |\mathbf{F}_{\alpha,i}|^2. \quad (14)$$

The potential energy in the PA case corresponds to a direct estimation of $V(r)$,

$$\frac{V_{\text{PA}}}{N} = \frac{1}{NM} \sum_{\alpha=1}^M \sum_{i < j}^N V(r_{\alpha,ij}), \quad (15)$$

whereas the application of Eq. (12) for the TIA produces the same additional force term of Eq. (14), multiplied by a factor of two,

$$\frac{V_{\text{TIA}}}{N} = \frac{V_{\text{PA}}}{N} + \frac{1}{12} \frac{\hbar^2}{m} \frac{\beta^2}{NM^3} \sum_{\alpha=1}^M \sum_{i=1}^N |\mathbf{F}_{\alpha,i}|^2. \quad (16)$$

The unbiased convergence of both the PA and TIA factorizations to the exact energy when M increases is granted by the Trotter formula.⁷ However, the thermodynamic estimator for both approaches (13,14) presents the drawback of a statistical variance which increases with the number of beads M .^{28,29} To overcome this problem one can derive another estimator for the energy by exploiting the invariance of the partition function under a rescaling of the particle positions ($\mathbf{r}_i \rightarrow \lambda \mathbf{r}_i$). This leads to the so called virial estimator²⁸ in which the kinetic energy is obtained from derivatives of the interatomic potential $V(r)$. It has been proved that, contrary to the thermodynamic estimator, the variance of the virial estimator is roughly constant as a function of M .^{28,29} We have chosen in the present work the centroid version of the virial estimator. In the PA,

$$\frac{K_{\text{PA}}^{\text{cv}}}{N} = \frac{3}{2\beta} + \frac{1}{2} \frac{1}{NM} \sum_{\alpha=1}^M \sum_{i=1}^N (\mathbf{r}_{\alpha,i} - \mathbf{r}_{0,i}) \cdot \mathbf{F}_{\alpha,i}, \quad (17)$$

with $\mathbf{r}_{0,i} = (\mathbf{r}_{1,i} + \dots + \mathbf{r}_{\alpha,i})/M$ the centroid position of atom i . By applying the same method to the TIA, two new terms appear requiring up to the second derivative of $V(r)$,

$$\frac{K_{\text{TIA}}^{\text{cv}}}{N} = \frac{K_{\text{PA}}^{\text{cv}}}{N} + \frac{1}{24} \frac{\hbar^2}{m} \frac{\beta^2}{NM^3} \sum_{\alpha=1}^M \sum_{i=1}^N \left\{ |\mathbf{F}_{\alpha,i}|^2 + \sum_{j \neq i}^N (r_{\alpha,i} - r_{0,i})^a T(\alpha, i, j)_a^b (F_{\alpha,i} - F_{\alpha,j})_b \right\}, \quad (18)$$

where $\{a, b\}$ stand for the Cartesian coordinates and an implicit summation over repeated indices has been assumed. The tensor T is explicitly written as

$$T(\alpha, i, j)_a^b = \left[\frac{\delta_a^b}{r_{\alpha,ij}} - \frac{(r_{\alpha,ij})^b (r_{\alpha,ij})_a}{r_{\alpha,ij}^3} \right] \frac{dV(r_{\alpha,ij})}{dr_{\alpha,ij}} + \frac{(r_{\alpha,ij})^b (r_{\alpha,ij})_a}{r_{\alpha,ij}^2} \frac{d^2V(r_{\alpha,ij})}{dr_{\alpha,ij}^2}. \quad (19)$$

The PIMC method is the most efficient theoretical tool to deal with a microscopic description of systems at low temperatures where quantum effects are unavoidable. With the only external assumption of the interatomic potentials, PIMC provides exact results at a given temperature with a self-contained adjustment of the number of terms (beads M) in the action to the *quanticity* of the system: from $M = 1$, which corresponds to classical Monte Carlo (each particle is a point in the configuration space), to values of M (each particle is represented by a closed chain of beads) larger enough to fulfill the Trotter formula.⁷ It is hence essential to remove from the calculation the bias coming from the use of a discrete value for M , or at least to reduce it to the level of the typical statistical error. In order to help in this analysis we have used the well-known Richardson extrapolation;²³ its use in numerical integration, derivation or differential equations permits to achieve high accuracy by using low-order formulas.

The M -dependence of integrated quantities like the energy for the PA and TIA, when $M \rightarrow \infty$, is of the form

$$E = E_0 + A_\delta \left(\frac{1}{M} \right)^\delta + A_{\delta+2} \left(\frac{1}{M} \right)^{\delta+2} + \dots, \quad (20)$$

with $\delta = 2, 4$ for PA and TIA, respectively. The value $1/M$ in PIMC plays the same role than the step size h in a numerical integration and in both cases one is interested in the extrapolation to the *ideal* case $h = 0$ ($1/M = 0$). Richardson extrapolation is a simple and clever way of performing that extrapolation improving the order of the approach. In the present case, the extrapolation to $M = \infty$ is given by

$$E_\infty^{(\delta)} = E_2 + \left\{ \frac{(M_1/M_2)^\delta}{1 - (M_1/M_2)^\delta} \right\} (E_2 - E_1), \quad (21)$$

E_1 and E_2 being the energies estimated using M_1 and M_2 beads, respectively ($M_2 > M_1$). When the calculation proceeds, and M is progressively increased it is also useful to know how far one is from the asymptotic law (20). In this respect, the Richardson extrapolation can also be used to predict the energy for a number of beads $M > M_2 > M_1$ through

$$E_M^{(\delta)} = E_1 + \left\{ \frac{1 - (M_1/M)^\delta}{1 - (M_1/M_2)^\delta} \right\} (E_2 - E_1) . \quad (22)$$

III. RESULTS

The usefulness of the Richardson extrapolation on top of the PIMC calculations and the accuracy of the TIA with respect to the PA have been studied in three different systems. The first one corresponds to the test problem of a particle in a one-dimensional harmonic potential in which the exact solution is known. In the second one, we study liquid Ne at 25.8 K, a real system at relatively high density and where the interatomic interaction presents a hard core at short distances. Finally, the most exigent test in the present analysis corresponds to the calculation of the energy of liquid ^4He at 5.1 K in which the low temperature, the small mass, and the hard core of the interactions make the quantum effects much larger.

The sampling of the three systems studied has been carried out by combining collective movements of some beads of a given chain and movements of the center of mass of each one of the chains representing the atoms. In both movements the size of the proposed movements is fixed to keep a Metropolis acceptance of 30-50%. As it has been proved, the introduction of multibead movements is unavoidable when the number of beads increases since they eliminate the slowing down observed in a bead by bead sampling. To this end, we have used the bisection^{2,13} and staging¹⁰⁻¹² methods: the bisection up to level three for short chains and staging for longer ones. Both methods correspond to an exact sampling of the free (kinetic) part of the action and therefore, in the Metropolis step, only the potential part of the action is sampled.

A. Harmonic oscillator

We consider a particle in a one-dimensional harmonic well with Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 . \quad (23)$$

In this problem, the partition function and the energy are exactly known,⁶

$$Z = [2 \sinh(\beta \hbar \omega / 2)]^{-1} \quad (24)$$

$$E = \frac{1}{2} \hbar \omega \coth(\beta \hbar \omega / 2) . \quad (25)$$

In the PIMC calculation we have assumed $\omega = \hbar = m = 1$, and $T = 0.2$. The exact energy from Eq. (25) at this temperature and using these reduced units is 0.50678.

In Table I, PIMC results obtained using the PA and TIA approximations are reported as a function of the number of beads M . As already known for this model problem,^{17,18} the accuracy of E_{TIA} is manifestly superior to the PA energies E_{PA} . Within a statistical fluctuation of 10^{-5} , PA arrives to the exact energy when $M = 512$ whereas TIA requires only $M = 32$, a figure sixteen times smaller. In the same Table, we report Richardson extrapolations to a given M ($E_M^{(\delta)}$, Eq. 22) and to $M \rightarrow \infty$ ($E_\infty^{(\delta)}$, Eq. 21), derived from calculated results (E_{PA} , E_{TIA}) using $M/4$ and $M/2$ beads. When $\delta = 2$, i.e., in the PA, the extrapolation to $M \rightarrow \infty$ achieves the asymptote with only $M = 64$, a factor of eight smaller than using only the direct output E_{PA} . The extrapolation to a next M is also helpful to

M	E_{PA}	$E_M^{(2)}$	$E_\infty^{(2)}$	E_{TIA}	$E_M^{(4)}$	$E_\infty^{(4)}$
2	0.30755			0.44702		
4	0.43162			0.50053		
8	0.48424	0.46264	0.47298	0.50630	0.50387	0.50410
16	0.50085	0.49740	0.50178	0.50675	0.50666	0.50668
32	0.50528	0.50500	0.50639	0.50678	0.50678	0.50678
64	0.50641	0.50639	0.50676	0.50678	0.50678	0.50678
128	0.50669	0.50669	0.50679		0.50678	0.50678
256	0.50676	0.50676	0.50678			
512	0.50678	0.50678	0.50678			
1024		0.50678	0.50679			

TABLE I: PA (E_{PA}) and TIA (E_{TIA}) results for the one-dimensional harmonic oscillator at $T = 0.2$. Richardson extrapolations to M ($E_M^{(\delta)}$) and to $M \rightarrow \infty$ ($E_\infty^{(\delta)}$), using the $M/4$ and $M/2$ energies, are also reported ($\delta = 2, 4$ stands for PA and TIA, respectively).

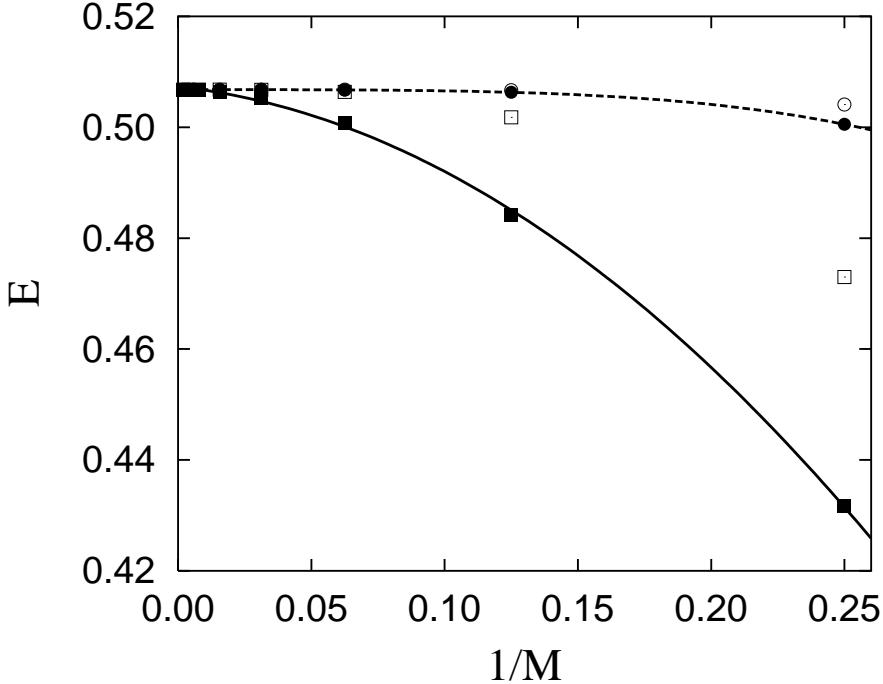


FIG. 1: PA (filled squares) and TIA (filled circles) results for the one-dimensional harmonic oscillator as a function of $1/M$. Solid and dashed lines are the fits (26) to the data. Open symbols stand for the Richardson extrapolations (squares, PA; circles, TIA).

know when the expected quadratic law is attained since there that extrapolation coincides with the direct PA calculation. Finally, in Table I, the Richardson extrapolations from TIA results are shown. In this case, the gain achieved by the extrapolation is significantly smaller since only a factor of two seems reachable.

The dependence of the PIMC results on the *step* $1/M$ is plotted in Fig. 1. As it is expected from the accuracy of the PA and TIA factorizations, the behavior of the energy when $1/M \rightarrow 0$ follows the power law

$$E = E_0 + A_\delta (1/M)^\delta , \quad (26)$$

with E_0 the exact energy and $\delta = 2, 4$ for PA and TIA, respectively. The lines in the Figure correspond to fits to the PIMC results when the power law (26) starts to be valid. As commented before, Richardson extrapolation is a good tool to establish the smaller value of M from which up PIMC results follow this asymptotic behavior. On the other hand, one can see in the same Figure the behavior of the extrapolated energies. The combination of the PA and Richardson extrapolation reduces dramatically the difference between PA and

M	$(V/N)_{\text{PA}}$	$(K/N)_{\text{PA}}$	$(E/N)_{\text{PA}}$	$(V/N)_{\text{TIA}}$	$(K/N)_{\text{TIA}}$	$(E/N)_{\text{TIA}}$
2	-210.25(12)	44.42(2)	-165.84(14)	-207.18(13)	48.04(4)	-160.14(16)
4	-208.30(16)	47.80(4)	-160.50(19)	-207.58(17)	49.43(5)	-158.15(22)
8	-207.80(17)	49.05(5)	-158.76(22)	-207.48(11)	49.61(3)	-157.87(13)
16	-207.56(17)	49.48(5)	-158.08(20)	-207.47(20)	49.71(6)	-157.76(22)
32	-207.52(22)	49.60(6)	-157.92(22)			
64	-207.51(44)	49.70(9)	-157.81(36)			

TABLE II: Total (E), kinetic (K), and potential (V) energies for a different number of beads M in liquid Ne at 25.8 K. Figures within brackets are the statistical errors.

TIA with zero computational cost.

B. Neon at 25.8 K

The first application to a real system corresponds to a PIMC simulation of liquid Ne at a experimental point of coordinates: temperature $T = 25.8$ K and density $\rho = 0.0363 \text{ \AA}^{-3}$. We have used a simulation box containing 108 particles with periodic boundary conditions to represent the homogeneous liquid. Finite size effects have been studied and proved to be well corrected by summing up to the energy standard tail corrections to the potential energy. The interatomic potential between Ne atoms is the HFD-B model proposed by Aziz *et al.*³⁰

The results obtained using the PA and TIA for the total and partial energies are reported in Table II for an increasing number of beads. The value of the kinetic energy, which is compatible with previous estimations reported in Refs. 31 and 32, is a good measure of the relevance of quantum effects. Subtracting the classical kinetic energy ($3T/2$) from the PIMC value, this quantum correction amounts 11 K to be compared with the total value reported in Table II, 49.7 K . Taking into account the statistical error bars, the total energy reaches its asymptotic value in terms of $1/M$ for $M = 32$ and $M = 8$ using the PA and the TIA, respectively. Therefore, M is reduced by a factor of four, a figure significantly smaller than the gain obtained in the harmonic oscillator. In spite of this decrease, it is still more

M	$(E/N)_{\text{PA}}$	$(E/N)_M^{(2)}$	$(E/N)_{\infty}^{(2)}$	$(E/N)_{\text{TIA}}$	$(E/N)_M^{(4)}$	$(E/N)_{\infty}^{(4)}$
2	-165.84(14)			-160.14(16)		
4	-160.50(19)			-158.15(22)		
8	-158.76(22)	-159.16(24)	-158.72(25)	-157.87(13)	-158.03(24)	-158.02(24)
16	-158.08(20)	-158.32(28)	-158.18(29)	-157.76(22)	-157.85(14)	-157.85(14)
32	-157.92(22)	-157.91(25)	-157.85(26)		-157.75(24)	-157.75(24)
64	-157.81(36)	-157.88(28)	-157.87(29)			
128		-157.78(45)	-157.77(47)			

TABLE III: Richardson extrapolations, to M ($(E/N)_M^{(\delta)}$) and to ∞ ($(E/N)_{\infty}^{(\delta)}$), of the total energy of liquid Ne with both, PA and TIA.

efficient to use the TIA than the PA since the computation time for getting the same level of statistical error using TIA is less than the one required with PA.

The usefulness of the Richardson extrapolation in this system is explored in Table III. Focusing the analysis on the PA action, in which the extrapolation is expected to be more useful, one can see how the extrapolated estimations approach the asymptote faster than the direct calculations: starting from $M = 16$ the energy remains constant inside the confidence interval determined by the statistical error. It is obvious that the unavoidable presence of statistical errors in a real calculation reduces the accuracy of the Richardson extrapolation. Nevertheless, it always improves the direct calculation and helps in determining the proximity to the expected power law (26). On the other hand, in the case of the TIA the extrapolation also improves the direct estimations but the gain is much smaller than in the PA.

The dependence of the PA and TIA energies on the $step 1/M$ is shown in Fig. 2. The lines correspond to fits (26) to the data when $1/M \rightarrow 0$ with $\delta = 2, 4$ for PA and TIA, respectively. From the numerical fitting, the final energy per particle is -157.846(20) K for the PA and -157.824(42) K for the TIA. The Figure also contains the Richardson extrapolations to $1/M \rightarrow 0$ from PA, which represent a significant improvement with respect the PA data and approach the fourth-order behavior of TIA.

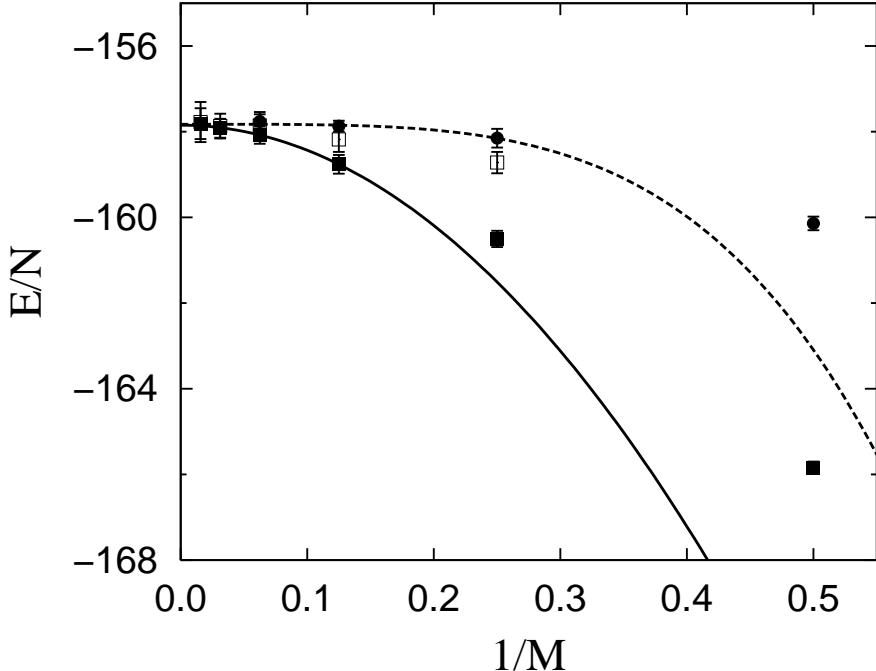


FIG. 2: PA (filled squares) and TIA (filled circles) energies for Ne at 25.8 K as a function of $1/M$. Solid and dashed lines are the fits (26) to the data. Open squares stand for the Richardson extrapolations using the PA data.

C. Liquid ^4He at 5.1 K

The third system studied in the present work is the more demanding one: liquid ^4He at 5.1 K and density $\rho = 0.02186 \text{ \AA}^{-3}$. As it is well known, liquid ^4He is the paradigm of a quantum Bose liquid and its properties have been well reproduced theoretically both at zero³³ and finite temperature.² At 5.1 K, ^4He is in its normal phase and the probability of accepting exchanges by introducing the correct symmetry in the action is very small, so its influence on the total energy becomes negligible.² Therefore, we consider ^4He atoms as Boltzmann-like particles. The interatomic potential is the HFD-B(HE) model from Aziz *et al.*,³⁴ used with high accuracy in zero-temperature calculations, and the homogeneous phase is simulated using a cubic box containing 64 atoms with periodic boundary conditions. Increasing the number of atoms, for a fixed number of beads, we have verified that the tail corrections added to the energy accounts satisfactorily for finite-size effects.

Table IV contains results for the total and partial energies for an increasing number of beads M . The essentially quantum nature of ^4He is reflected in the high value of its kinetic

M	$(V/N)_{\text{PA}}$	$(K/N)_{\text{PA}}$	$(E/N)_{\text{PA}}$	t_{PA}	$(V/N)_{\text{TIA}}$	$(K/N)_{\text{TIA}}$	$(E/N)_{\text{TIA}}$	t_{TIA}
8	-23.955(15)	14.663(15)	-9.292(20)	0.8	-22.803(10)	16.503(25)	-6.300(26)	2.7
16	-22.737(10)	16.885(20)	-5.852(23)	1.5	-22.124(12)	18.157(25)	-3.967(26)	4.5
32	-22.162(13)	18.180(23)	-3.982(27)	3.3	-21.895(12)	18.852(26)	-3.043(27)	9.9
64	-21.940(16)	18.754(23)	-3.186(25)	9.2	-21.846(14)	18.996(26)	-2.850(27)	26.1
128	-21.870(18)	18.951(24)	-2.919(26)	17.1	-21.850(14)	19.027(27)	-2.823(28)	51.9
256	-21.848(17)	19.006(23)	-2.842(25)	40.5				
512	-21.843(20)	19.036(30)	-2.807(32)	82.4				

TABLE IV: Total (E), kinetic (K), and potential (V) energies for a different number of beads M in liquid ${}^4\text{He}$ at 5.1 K. t_{PA} (t_{TIA}) is the CPU time in thousands of seconds of a PIV-2.4GHz computer using the PA (TIA) approximation.

M	$(E/N)_{\text{PA}}$	$(E/N)_M^{(2)}$	$(E/N)_{\infty}^{(2)}$	$(E/N)_{\text{TIA}}$	$(E/N)_M^{(4)}$	$(E/N)_{\infty}^{(4)}$
8	-9.292(20)			-6.300(26)		
16	-5.852(23)			-3.967(26)		
32	-3.982(27)	-4.992(29)	-4.705(31)	-3.043(27)	-3.821(28)	-3.811(28)
64	-3.186(25)	-3.514(34)	-3.359(36)	-2.850(27)	-2.985(29)	-2.981(29)
128	-2.919(26)	-2.987(31)	-2.921(33)	-2.823(28)	-2.838(29)	-2.837(29)
256	-2.842(25)	-2.852(33)	-2.830(35)		-2.821(30)	-2.821(30)
512	-2.807(32)	-2.823(31)	-2.816(33)			
1024		-2.798(40)	-2.795(43)			

TABLE V: Richardson extrapolations, to M ($(E/N)_M^{(\delta)}$) and to ∞ ($(E/N)_{\infty}^{(\delta)}$), of the total energy of liquid ${}^4\text{He}$ with both, PA and TIA.

energy, comparable to the potential energy. The quantum correction on top of the classical value is ~ 11.5 K, to be compared with a total value of 19.0 K. Regarding the behavior of the PA and TIA energies with M , one can observe a similar behavior to the one obtained for Ne in the previous Subsection. The asymptotic value using PA is reached for $M = 256$ whereas $M = 64$ for the TIA; the accuracy is then improved by a factor of four. Considering

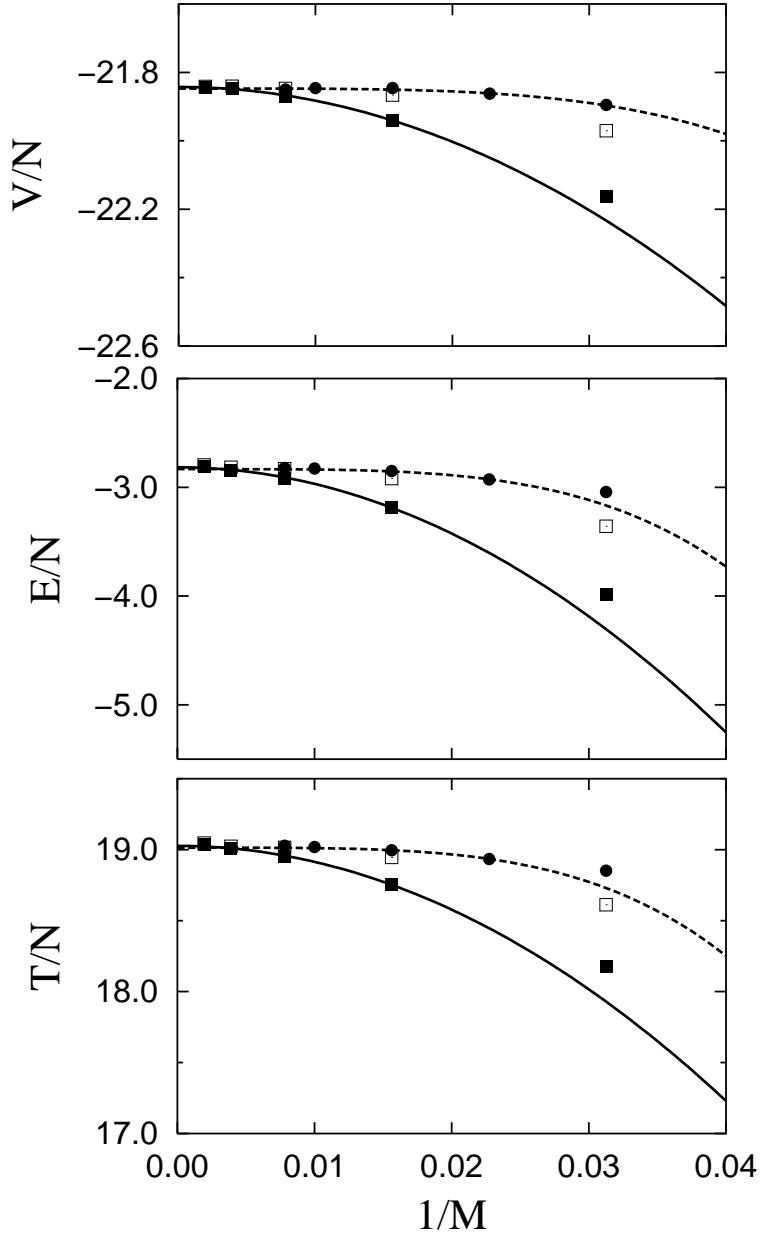


FIG. 3: Potential, total, and kinetic energies of liquid ^4He at 5.1 K. PA and TIA data are shown as filled squares and filled circles, respectively. Solid and dashed lines are the fits (26) to the data. Open squares stand for the Richardson extrapolations using the PA data.

altogether, the reduction in the number of beads and the additional computation required for the TIA, the efficiency of the TIA is still greater than the one of the PA.

Richardson extrapolations using the PIMC results for the total energies are reported in Table V. The main features are common to the ones observed in Ne. The use of Richardson extrapolation always improves the direct calculation with zero computational cost and it

arrives faster to the asymptote. From the results contained in the Table, one can see that the right energy using PA is obtained with data up to $M = 128$, a factor of two smaller than the direct PA calculation. In the case of the TIA, the extrapolation is also better than the direct output but it does not significantly improve the efficiency in achieving the plateau.

Figure 3 is a plot of the total and partial energies as a function of $1/M$ near the region where the power laws (26) are satisfied. As it can be seen, the TIA data approaches the limit according to a fourth-order law, a point that sometimes has been questioned for hard-core-like interactions at very low temperatures. The Richardson extrapolations make a good job for both the total and partial energies by improving significantly the $1/M$ dependence of the PA data. An unbiased estimation of the energies is drawn from the numerical fits (26) with $\delta = 2$ for PA and 4 for TIA. Using PA, $K/N = 19.026(7)$ K, $V/N = -21.842(2)$ K, and $E/N = -2.816(8)$ K. With the TIA, $K/N = 19.019(6)$ K, $V/N = -21.847(3)$ K, and $E/N = -2.827(5)$ K. At the same thermodynamic point, Ceperley and Pollock³⁵ reported a total energy of -2.61 K and a kinetic energy of 18.09 K, but using a different interatomic potential.

IV. CONCLUSIONS

In the present work we have explored two possible strategies for improving the number-of-beads-dependence of the PIMC algorithm, specially for exigent problems in which the use of PA may require a very large number M . First, the usefulness of the Richardson extrapolation on top of the PA data has been analyzed for the first time. Richardson extrapolation is a clever way of practically improving the order of the errors introduced by discretization and its use in numerical algorithms like integration or solution of differential equations is widely known. Also in PIMC a discretization through an effective step $1/M$ is introduced and one is interested in going to the limit $1/M \rightarrow 0$. The results obtained have proved that also in PIMC Richardson extrapolation can be useful since it approaches faster to the asymptote and helps to know when the discrete results behave according to the expected power law. It is worth mentioning that the presence of statistical errors mask somewhat the signal but it is also true that the computational cost of the extrapolation is certainly zero.

The second main focus of the work has been to study the behavior of the TIA in systems with hard-core-like interactions and well into the quantum regime. Previous tests of the

TIA^{24–27} were performed in less exigent conditions and some doubts concerning the fail of the predicted fourth-order accuracy were formulated. The present results, mainly the ones achieved in the calculation of ${}^4\text{He}$, have shown that the fourth order law is maintained. On the other hand, the TIA introduces in the calculation additional computation due to the need of the second derivative of the potential (using the virial estimator for the kinetic energy, absolutely necessary when M increases). This is not a serious problem, at least when empirical potentials are used, and the computer time to achieve the same statistical error in the asymptotic limit in M is ever reduced. Our present experience shows that the CPU time is at least a 30% smaller, and that this percentage increases with the number of beads required to reach the asymptote.

As a final point, the fact that the double commutator $[[V, K], V]$ in the TIA has allowed for a substantial decrease of the systematic errors for very different potentials is an encouraging result. At present, Chin²² is developing various families of symplectic algorithms in which that double commutator originates a fourth-order correction which can be fine-tuned both in sign and magnitude. This bears the promise of achieving an effective cancellation of the leading fourth and sixth order corrections, feature which could result in a dramatic reduction of the computational cost of PIMC calculations. Further work in this direction would be most interesting.

Acknowledgments

This work was supported, in part, by the DGI (Spain) Grant No. BFM2002-00466, Generalitat de Catalunya Grant No. 2001SGR-00222, and project MIUR-2001/025/498 (Italy).

¹ M. J. Gillan, in *Computer Modelling of Fluids, Polymers and Solids*, edited by C. R. A. Catlow *et al.* (Kluwer, Dordrecht, 1990).

² D. M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995).

³ C. Chakravarty, Int. Rev. Phys. Chem. **16**, 421 (1997).

⁴ R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).

- ⁵ R. P. Feynman, *Statistical Mechanics* (Benjamin, New York, 1972).
- ⁶ H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, and Polymer Physics* (World Scientific, Singapore, 1995).
- ⁷ H. F. Trotter, Proc. Am. Math. Soc. **10**, 545 (1959).
- ⁸ J. Barker, J. Chem. Phys. **70**, 2914 (1979).
- ⁹ D. Chandler and P. G. Wolynes, J. Chem. Phys. **74**, 4078 (1981).
- ¹⁰ E. L. Pollock and D. M. Ceperley, Phys. Rev. B **30**, 2555 (1984).
- ¹¹ M. Sprik, M. L. Klein, and D. Chandler, Phys. Rev. B **31**, 4234 (1985); *ibid*, **32**, 545 (1985).
- ¹² M. E. Tuckerman, B. J. Berne, G. J. Martyna, and M. L. Klein, J. Chem. Phys. **99**, 2796 (1993).
- ¹³ C. Chakravarty, M. C. Gordillo, and D. M. Ceperley, J. Chem. Phys. **109**, 2123 (1998).
- ¹⁴ H. D. Raedt and B. D. Raedt, Phys. Rev. A **28**, 3575 (1983).
- ¹⁵ R. M. Fye, Phys. Rev. B **33**, 6271 (1986).
- ¹⁶ J. D. Doll, D. L. Freeman, and T. L. Beck, Adv. Chem. Phys. **78**, 61 (1990).
- ¹⁷ M. Takahashi and M. Imada, J. Phys. Soc. Jpn. **53**, 3765 (1984).
- ¹⁸ X. P. Li and J. Q. Broughton, J. Chem. Phys. **86**, 5094 (1987).
- ¹⁹ S. Jang, S. Jang, and G. A. Voth, J. Chem. Phys. **115**, 7832 (2001).
- ²⁰ M. Suzuki, in *Computer Simulation Studies in Condensed Matter Physics VIII*, edited by D. P. Landau *et al.* (Springer-Verlag, New York, 1995).
- ²¹ S. A. Chin, Phys. Lett. A **226**, 344 (1997).
- ²² S. A. Chin and C. R. Chen, J. Chem. Phys. **117**, 1409 (2002).
- ²³ W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN. The art of scientific computing* (Cambridge University Press, 1999), chap. 16.4, 2nd ed.
- ²⁴ F. R. Krajewski and M. H. Müser, Phys. Rev. B **65**, 174304 (2002).
- ²⁵ D. J. Lacks, Phys. Rev. B **56**, 13927 (1997).
- ²⁶ R. O. Weht, J. Kohanoff, D. A. Estrin, and C. Chakravarty, J. Chem. Phys. **108**, 8848 (1998).
- ²⁷ K. Singer and W. Smith, Mol. Phys. **64**, 1215 (1998).
- ²⁸ M. F. Herman, E. J. Bruskin, and B. J. Berne, J. Chem. Phys. **76**, 5150 (1982).
- ²⁹ W. Janke and T. Sauer, J. Chem. Phys. **107**, 5821 (1997).
- ³⁰ R. A. Aziz and M. J. Slaman, Chem. Phys. **130**, 187 (1989).
- ³¹ M. C. S. D. A. Peek, I. Fujita, and R. O. Simmons, Phys. Rev. B **45**, 9671 (1992).

- ³² H. R. Glyde, R. T. Azuah, K. H. Andersen, and W. G. Stirling, in *Condensed matter theories*, edited by M. Casas *et al.*, (Nova Science Publishers, New York, 1995), vol. 10.
- ³³ J. Boronat, in *Microscopic approaches to Quantum Liquids in Confined Geometries*, edited by E. Krotscheck and J. Navarro (World Scientific, Singapore, 2002).
- ³⁴ R. A. Aziz, F. R. W. McCourt, and C. C. K. Wong, Mol. Phys. **61**, 1487 (1997).
- ³⁵ D. M. Ceperley and E. L. Pollock, Phys. Rev. Lett. **56**, 351 (1986).